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REACTION OF HEXAMETHYLDITIN WITH DIMETHYLTIN DICHLORIDE

I. PRODUCT COMPOSITION AND INTERMEDIATES

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Summary

Hexamethylditin in methanol solution reacts with dimethyltin dichloride to yield as major products trimethyltin chloride and polymeric materials whose composition depends upon the molar ratio of the reactants. Tetramethylditin dichloride is a significant minor product together with small amounts of various intermediates which have been tentatively identified. The stoichiometry of the reaction has been established.

Introduction

The reaction of one equivalent of $(CH_3)_2SnCl_2$ with two equivalents $(CH_3)_6Sn_2$ in methanol solution has been studied by Tagliavini, Pilloni and Plazzogna [1], who reported that yellow "dimethyltin" polymer is produced together with $(CH_3)_3SnCl$ and, at a later stage, $(CH_3)_4Sn$. Similar yellow products are obtainable from the $(CH_3)_6Sn_2$ + $(CH_3)_3SnCl$ reaction also studied by these workers [2] and by ourselves [3—5]. The present study was initiated for the purpose of reaction rate comparison, but many additional features were revealed.

The product composition, particularly the nature of the precipitated polymer, varies with the initial concentrations of the reactants, and a number of intermediates involved in concurrent reactions are observable in the system. A detailed study of the product compositions, the intermediates present and the stoichiometry of the system was hence essential prior to any kinetic studies.

Experimental

Materials

Hexamethylditin was prepared using a method based upon that of Kraus and Sessions [6], i.e.

$$2(CH_3)_3SnCl + 2\ Na \rightarrow (CH_3)_6Sn_2 + 2\ NaCl$$

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Liquid ammonia (ca. 200 ml) was condensed into a 500 ml three-necked flask fitted with nitrogen inlet, drying tube and mechanical stirrer and immersed in a dry ice/acetone bath at —78°C. To this was added $(CH_3)_3SnCl$ (12.2 g, 0.06 mol) and, subsequently, 1.41 g (0.06 mol) of sodium sand over a period of one hour. The mixture was stirred at —78°C for three hours and then allowed to warm to room temperature under a strong stream of N_2. After all of the ammonia had evaporated, the residual cake of white solid was treated with moist ether (200 ml) followed by water (50 ml). The ether layer was further washed with water, separated and dried over anhydrous sodium sulphate. The ether was removed at reduced pressure and the product distilled at low pressure under nitrogen (b.p. 99—102°C/55 mmHg). Yield = 7.2 g $(CH_3)_6Sn_2$ (71.8%).

To ensure maximum purity of $(CH_3)_6Sn_2$ the above product was further distilled under N_2 in the short-path distillation apparatus. This final distillation removed an unidentified oxidation product present in the $(CH_3)_6Sn_2$. (In our previous work [7,8], we had been unable to achieve this purification.) Small portions (ca. 0.6 g) were distilled at a time with fractions (ca. 0.2 g each) being collected in small tubes, sealed under vacuum and stored at —25°C.

Perdeutero-tetramethyltin was prepared following the method of Edgell and Ward [9] but using a smaller excess of Grignard reagent. A yield of 4.7 g (82%) was obtained using trideutero-methyl iodide (20 g, 0.14 mol), magnesium (3.6 g, 0.15 mol) and stannic chloride (7.8 g, 0.03 mol) in dry di-n-butyl ether.

Perdeutero-trimethyltin chloride was obtained from a redistribution reaction [10] of perdeutero-tetramethyltin (1.15 g, 0.006 mol) with stannic chloride (0.52 g, 0.002 mol). When the mixture was heated for two hours at ca. 150°C, allowed to cool and distilled from the reaction vessel, 1.55 g (93%) of product were collected at 75—76°C/45 mmHg. Perdeuterodimethyltin dichloride was prepared from perdeutero-tetramethyltin by the redistribution reaction with an equimolar quantity of stannic chloride at 140°C (3 h) [10]. The crude product was recrystallized from hexane and resublimed at 100°C/80 mmHg. The yield of pure material (m.p. 108—109.5°C) from 1.20 g (6.29 mmol) $(CD_3)_4Sn$ and 1.64 g (6.29 mmol) $SnCl_4$ was 2.40 g (85%). Undeuterated tetramethyltin, trimethyltin chloride and dimethyltin dichloride were prepared in similar fashion.

Methanol was AJAX UNIVAR for non-aqueous titrations which was further dried by the method of Lund and Bjerrum [11].

Methyl-d_3 iodide was obtained from Koch-Light and di-n-butyl ether from Unilab (dried by stirring with granulated $CaCl_2$ for 2 days followed by fractional distillation and stored over molecular sieves (Type 4A).

Product examination

Reactions were carried out either in NMR tubes sealed with pressure caps and studied by NMR spectroscopy, or, when the polymeric product was required, in foil wrapped flasks closed with septum caps under nitrogen. In the latter case the supernatant liquid removed by syringe and the precipitate washed several times with cold, dry methanol before collection by filtration under nitrogen.

^1H NMR spectra were recorded at 100 MHz (JEOL PS-100 in the CW mode or FX-100 in the FT mode) and ^{13}C NMR spectra at 25.05 MHz (FX-100) at 30 (±0.5)°C.

Concentrations at all times except $t = 0$ were determined from the heights of ^{1}H NMR resonances, although the area under a peak is a more correct measure. The use of integrals is rendered impossible by the number and proximity of signals in any spectrum. However, except where line broadening occurs, all of the resonances are sharp singlets arising from methyl groups in similar compounds, and the more practical technique of peak height measurement has been shown to be quite valid by the analyses of standard sample by previous workers in this laboratory [7,8], provided the spectrometer is maximally tuned. It has been assumed that when peaks are broadened, the peak shape is maintained such that if a peak of height h^0 and width w^0 is broadened to width w' and height h' then the 'unbroadened' height h^0 may be determined as $h^0 = w'h'/w^0$.

Careful study of expanded spectra showed that perturbation of the shape of $(CH_3)_4Sn_2Cl_2$ resonance is very slight. When the $(CH_3)_2SnCl_2$ resonance has become very broad, however, a somewhat more pronounced shape distortion is observed, but direct determination of the concentration of $(CH_3)_2SnCl_2$ was not needed for the kinetic and stoichiometric analyses undertaken (see below).

It is necessary to apply certain corrections before a peak height can be used as a measure of concentration. Firstly, all heights in a spectrum were divided by the height of the cyclohexane resonance to correct for adjustments made to the spectrometer gain controls during the course of the experiment. Then, all relative heights are divided by the number of methyl groups represented thereby. Further corrections are necessary for the contribution of ^{13}C, and ^{115,117,119}Sn satellites to a total resonance. Thus in the signal of a methyl group attached to one tin atom the central resonance corresponds to only magnetically inactive tin and carbon, i.e. to 83.3% of the tin and 98.9% of the carbon. The ratio of central resonance to total resonance is then $(0.833 \times 0.989) = 0.824 : 1$ and when two tin atoms couple to the protons of a methyl group, the ratio becomes $(0.833 \times 0.833 \times 0.989) = 0.686 : 1$.

Mass spectra were recorded by Mr. G. McFarlane at 70 eV on an A.E.I. MS 902S instrument. In cases where fragments at $m/e >$ ca. 800 were produced it was necessary to expand the range by employing an accelerating voltage of 4 kV rather than the normal 8 kV.

Results and discussion

It was found that systematic variation of the initial concentrations of reactants has a pronounced effect on the course of reaction. When the initial molar ratio of $(CH_3)_2SnCl_2$: $(CH_3)_6Sn_2$ is less than 2 : 1, a copious yellow polymeric precipitate appears, as reported previously [1]. If, however, greater than two equivalents of $(CH_3)_2SnCl_2$ are employed, a much smaller quantity of a greasy, off-white precipitate is obtained. The use of three or more equivalents of $(CH_3)_2SnCl_2$ gives rise, during the later stages of reaction, to a precipitate of metallic tin.

A sample of the yellow polymer precipitated from a reaction mixture comprised of $(CH_3)_2SnCl_2$ (0.23 *M*) and $(CH_3)_6Sn_2$ (0.23 *M*) was collected and its mass spectrum is detailed in Table 1 for the ions containing three or more tin atoms. (Each ion reported is the largest peak of a set due to the various isotopes whose pattern is characteristic of the number of tin atoms).

TABLE 1

MASS SPECTRUM OF YELLOW POLYMER EX $(CH_3)_2SnCl_2$: $(CH_3)_6Sn_2$ = 1 : 1

m/e	Probable ion	Relative intensity	m/e	Probable Ion	Relative intensity
922	$(CH_3)_{14}Sn_6^{+\cdot}$	1.4	596	$(CH_3)_8Sn_4^{+\cdot}$	15.1
907	$(CH_3)_{13}Sn_6^{+}$	0.8	581	$(CH_3)_7Sn_4^{+}$	6.2
892	$(CH_3)_{12}Sn_6^{+\cdot}$	1.1	551	$(CH_3)_5Sn_4^{+}$	4.2
877	$(CH_3)_{11}Sn_6^{+}$	1.1	521	$(CH_3)_3Sn_4^{+}$	3.1
774	$(CH_3)_{12}Sn_5^{+}$	2.9	506	$(CH_3)_2Sn_4^{+\cdot}$	2.9
759	$(CH_3)_{11}Sn_5^{+}$	7.5	476	$(CH_3)_8Sn_3^{+\cdot}$	39.1
744	$(CH_3)_{10}Sn_5^{+\cdot}$	3.2	461	$(CH_3)_7Sn_3^{+}$	100.0
729	$(CH_3)_9Sn_5^{+}$	3.4	446	$(CH_3)_6Sn_3^{+\cdot}$	44.9
699	$(CH_3)_7Sn_5^{+}$	0.8	431	$(CH_3)_5Sn_3^{+}$	18.2
659	$C_5H_5Sn_5^{+}$	0.9	415	$C_4H_{11}Sn_3^{+}$	10.3
626	$(CH_3)_{10}Sn_4^{+\cdot}$	14.0	386	$(CH_3)_2Sn_3^{+}$	12.6
611	$(CH_3)_9Sn_4^{+}$	28.5	356	Sn_3^{+}	7.7

This spectrum is very similar to those of yellow precipitates from reaction of $(CH_3)_6Sn_2$ with $(CH_3)_3SnCl$ [5] and $(CH_3)_4Sn_2Cl_2$ [12]. In particular no chloride-containing fragments are observed, and this product is, then, also a mixture of compounds of general formula $(CH_3)_{2n+2}Sn_n$ (with perhaps some $(CH_3)_{2n}S_n$).

Considerable contrast is afforded by a white polymer obtained by reacting 0.22 *M* $(CH_3)_6Sn_2$ with 0.47 *M* $(CH_3)_2SnCl_2$. This greasy, semi-solid material was found to be extremely sensitive to light and heat, readily decomposing to metallic tin. Exposure to air for only brief periods results in the formation of a white, high melting powder of exceptionally poor solubility. (This was assumed

TABLE 2

MASS SPECTRUM OF WHITE POLYMER EX $(CH_3)_2SnCl_2$: $(CH_3)_6Sn_2$ ~ 2 : 1

(i) Fragments containing 2 or more Sn stoms

m/e	Probable ion	Intensity	m/e	Probable ion	Intensity
754	$(CH_3)_6Sn_5Cl_2^{+}$	42.1	481	$(CH_3)_6Sn_3Cl^{+}$	33.6
734	$(CH_3)_7Sn_5Cl^{+}$	27.1	465	$C_5H_{14}Sn_3Cl^{+}$	15.4
719	$(CH_3)_6Sn_5Cl^{+}$	10.4	421	$(CH_3)_2Sn_3Cl^{+}$	13.2
697	$C_5H_8Sn_5Cl^{+}$	2.7	401	$(CH_3)_3Sn_3^{+}$	5.3
599	$C_6H_{16}Sn_4Cl^{+}$	1.2	353	$(CH_3)_3Sn_2Cl_2^{+}$	65.9
555	$C_3H_8Sn_4Cl^{+}$	4.2	333	$(CH_3)_4Sn_2Cl^{+}$	100.0
535	$C_4H_{11}Sn_4^{+}$	17.6	317	$C_3H_8Sn_2Cl^{+}$	55.5
518	$(CH_3)_6Sn_3Cl_2^{+}$	94.8	287	$CH_2Sn_2Cl^{+}$	27.3
503	$(CH_3)_5Sn_3Cl_2^{+}$	26.8			

(ii) Fragments containing one Sn atom

m/e	Probable ion	Intensity	m/e	Probable ion	Intensity
(333)	$((CH_3)_4Sn_2Cl^{+})$	(0.5)	155	$SnCl^{+}$	53.7
220	$(CH_3)_2SnCl_2^{+\cdot}$	10.7	150	$(CH_3)_2Sn^{+}$	4.4
205	$CH_3SnCl_2^{+}$	100.0	135	CH_3Sn^{+}	12.7
185	$(CH_3)_2SnCl^{+}$	50.6	134	CH_2Sn^{+}	3.4
170	CH_3SnCl^{+}	6.7	121	HSn^{+}	2.6
165	$(CH_3)_3Sn^{+}$	14.7	120	Sn^{+}	17.0

TABLE 3

COMPARISON OF MASS SPECTRA OF $(CH_3)_4Sn_2Cl_2$ AND $(CH_3)_6Sn_2$

Fragment type	$(CH_3)_4Sn_2Cl_2$		$(CH_3)_6Sn_2$	
	Fragment	Intensity	Fragment	Intensity
M^+	$(CH_3)_4Sn_2Cl_2^{+\cdot}$	4.0	$(CH_3)_6Sn_2^{+\cdot}$	10.7
$(M - CH_3)^+$	$(CH_3)_3Sn_2Cl_2^+$	34.0	$(CH_3)_5Sn_2^+$	39.8
$(M - Cl)^+$	$(CH_3)_4Sn_2Cl^+$	16.0		
$(M - 3\ CH_3)^+$	$CH_3Sn_2Cl_2^+$	4.0	$(CH_3)_3Sn_2^+$	2.4
$(M - (CH_3)_2Sn)$	$(CH_3)_2SnCl_2^{+\cdot}$	15.0	$(CH_3)_4Sn^{+\cdot}$	0.0
	$(CH_3)_3Sn^+$	100.0	$(CH_3)_3Sn^+$	100.0

to be a mixture of organotin oxides and alkoxides). The mass spectrum of the white polymer (detailed in Table 2) consists almost entirely of fragments containing chlorine. The spectrum is, significantly, quite similar to that of the white precipitate formed in the "decomposition" of $(CH_3)_4Sn_2Cl_2$ in methanol solution [12]. It features a far greater preponderance of fragments containing only one tin atom that any spectrum of a yellow polymer. As these may arise, in part, from traces of reactants not removed in isolation of the precipitate, they are listed separately in Table 2. (Note that $(CH_3)_4Sn_2Cl^+$, the most abundant fragment containing more than one tin atom, is only 0.5% as intense as the most abundant monotin fragment $CH_3SnCl_2^+$).

It seems that the white polymer is a mixture of long-chain chlorinated methylpolystannanes $(CH_3)_{2n+2-m}Sn_nCl_m$ (mono- and dichlorocompounds predominant). These compounds seem to give rise to molecular ions of somewhat lower stability than those of their counterparts containing only methyl substituents.

Mathisch [13] has reported the mass spectrum of $(CH_3)_4Sn_2Cl_2$ and the intensities of various fragments observed, together with those of analogous fragments generated by $(CH_3)_6Sn_2$, are listed in Table 3. It is interesting to note that the spectrum of $(CH_3)_4Sn_2Cl_2$ features a reasonably intense $(CH_3)_2SnCl_2^+$ fragment (which presumably arises from the molecular ion by loss of $(CH_3)_2Sn$) and, more importantly, that the base peak is the ion rearrangement product $(CH_3)_3Sn^+$. Mathiasch reports no daughter ions which might arise from loss of HCl. However, in the spectra of compounds $(CH_3)_{2n+2-m}Sn_nCl_m$ 'proton-deficient' fragments such as $C_6H_{16}Sn_4Cl^+$, $C_3H_8Sn_4^+$ and $C_5H_{14}Sn_3Cl^+$ (corresponding to, respectively, $C_6H_{18}Sn_4CH_3^+$, $C_3H_9Sn_4CH_3^+$, $C_4H_{12}Sn_4^+$ and $C_5H_{15}Sn_3CH_3^+$ for the $(CH_3)_{2n+2}Sn_n$ series) suggest that loss of HCl may well be an important fragmentation.

Analysis of the species in solution prior to the appearance of precipitate was achieved by ^1H NMR spectroscopy. The spectrum of a typical reaction mixture is shown in Fig. 1 and indexed in Table 4.

The principal products, $(CH_3)_3SnCl$, $(CH_3)_4Sn$ and $(CH_3)_4Sn_2Cl_2$ are immediately identifiable from their chemical shifts and coupling constants. The remaining resonances, assigned to "telomer", are examined more fully below. Further verification was sought using ^{13}C NMR. A spectrum taken during the later stages of a reaction is shown in Fig. 2 and indexed in Table 5.

A feature of both ^1H and ^{13}C NMR spectra of this reaction system is a pronounced broadening of both the central resonance and the $^{117,119}Sn$ satellites of

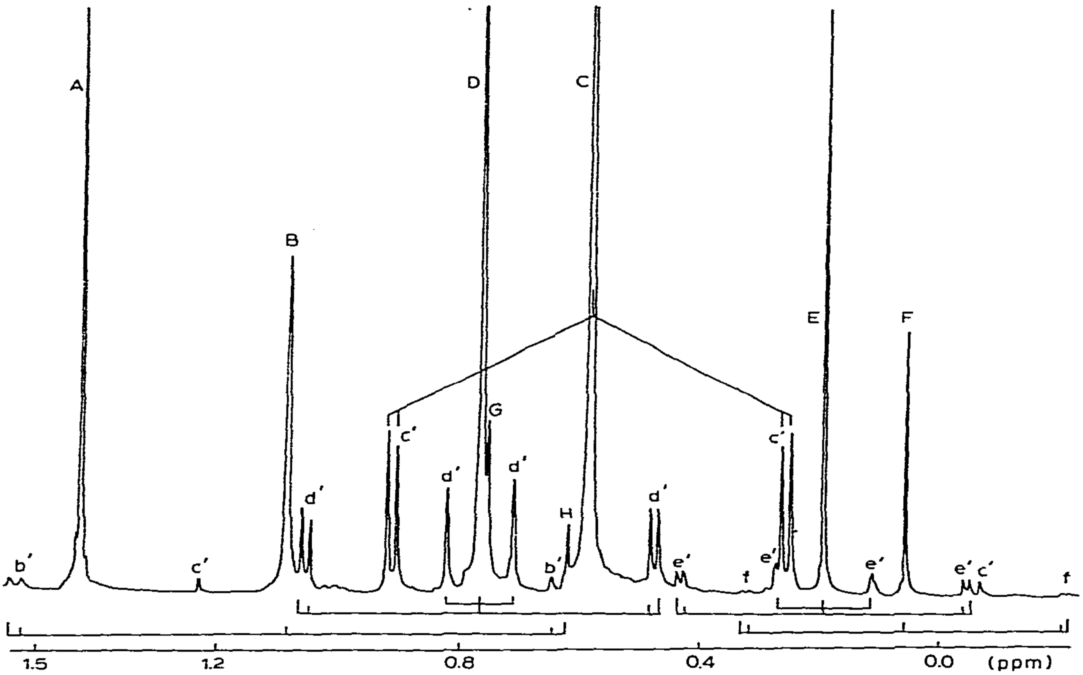


Fig. 1. ^1H NMR spectrum of reaction mixture: $(CH_3)_2SnCl_2$ (0.47 *M*) + $(CH_3)_6Sn_2$ (0.22 *M*) after 30 min.

the $(CH_3)_2SnCl_2$ signal. In ^1H spectra, this broadening is conspicuous even at quite early stages of reaction and is indicative of the involvement of $(CH_3)_2SnCl_2$ in an exchange process. This feature is examined in detail in the following paper [14].

For detailed kinetic analysis of this system it would clearly be appropriate to follow the change in concentration of $(CH_3)_2SnCl_2$, but to do this some account must be taken of this line-broadening. The techniques used in this determination, together with various conclusions concerning the nature of the exchange processes occurring, are set out below.

TABLE 4

REACTION MIXTURE: $(CH_3)_2SnCl_2$ (0.47 *M*) + $(CH_3)_6Sn_2$ (0.22 *M*) AFTER 30 MINUTES [a]

Peak	Chemical Shift (ppm)	^2J(Sn—H) (Hz)	^3J(Sn—H) (Hz)	Identity
A	1.45			cyclohexane
B	1.13	89.2, 92.9		$(CH_3)_2SnCl_2$
C	0.60	64.7, 67.8		$(CH_3)_3SnCl$
D	0.78	57.2, 59.8	11.1	$(CH_3)_4Sn_2Cl_2$
E	0.21	47.0, 49.0	15.7, 16.3	$(CH_3)_6Sn_2$
F	0.06	52.1, 54.6		$(CH_3)_4Sn$
G	0.76			"telomer"
H	0.63			"telomer"

[a] The resonances in Fig. 1, labelled c' etc. are the satellite peaks arising from ^{117}Sn and $^{119}Sn—^1H$ coupling; and those labelled c'' arise from $^{13}C—^1H$ coupling.

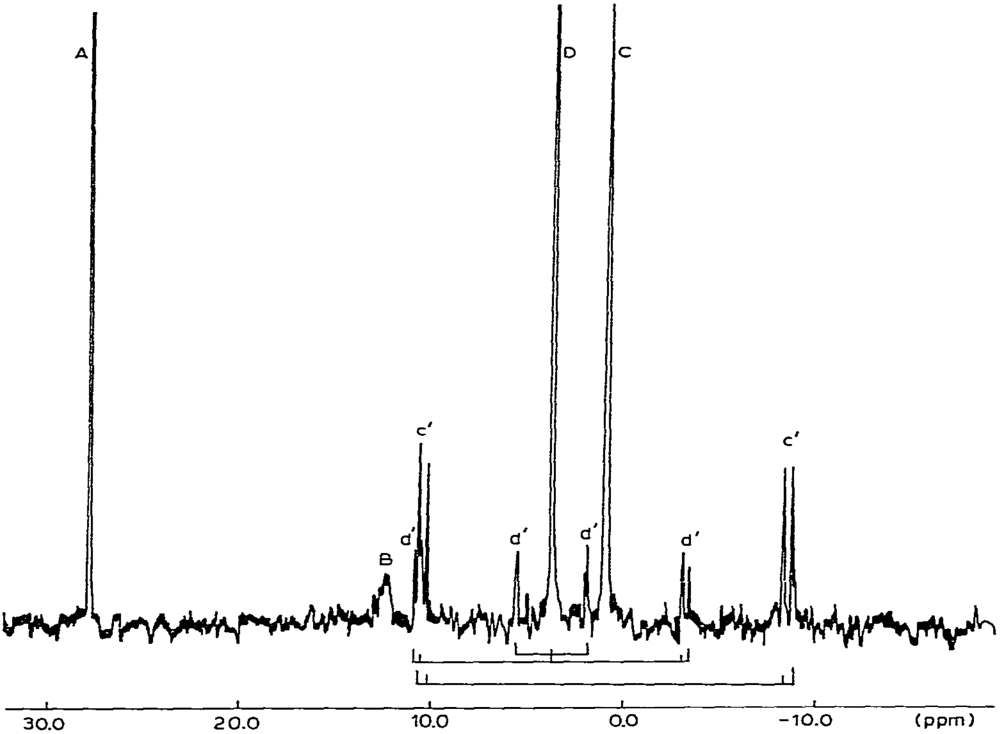


Fig. 2. ^{13}C NMR spectrum of reaction mixture: $(CH_3)_2SnCl_2$ + $(CH_3)_6Sn_2$.

Stoichiometry of reaction

The main products observed early in the reaction are $(CH_3)_3SnCl$, $(CH_3)_4Sn_2Cl_2$ and $(CH_3)_4Sn$ along with small amounts of "telomer" in solution. It is important that this analysis be confirmed and the stoichiometry of the reactions established. This can be achieved, in early stages of reaction before precipitation has commenced and while the quantity of "telomer" in solution is small, from considerations of the conservation of Sn, Cl and CH_3 groups in the system.

If at time $t = 0$ the solution contains E^0 mol of $(CH_3)_6Sn_2$ and B^0 mol of $(CH_3)_2SnCl_2$; and at $t = t$ it contains E mol $(CH_3)_6Sn_2$, B mol $(CH_3)_2SnCl_2$, C

TABLE 5

^{13}C NMR SPECTRUM OF REACTION MIXTURE $(CH_3)_2SnCl_2$ (0.20 *M*) + $(CH_3)_6Sn_2$ (0.08 *M*) AFTER 2 DAYS (ALL PRECIPITATE FILTERED OFF)

Peak	Chemical Shift (ppm)	^1J(Sn—C) (Hz)	^2J(Sn—C) (Hz)	Identity
A	27.84			cyclohexane
B	13.10	[a]		$(CH_3)_2SnCl_2$
C	0.91	468.3, 490.2		$(CH_3)_3SnCl$
D	3.71	343.3, 358.9	89.8, 94.2	$(CH_3)_4Sn_2Cl_2$

[a] Not observed here. Measured separately as 722.6, 755.9 Hz.

mol $(CH_3)_3SnCl$, F mol $(CH_3)_4Sn$ and D mol $(CH_3)_4Sn_2Cl_2$, then:

The solution contains

At $t = 0$	At $t = t$	
$6E^0 + 2B^0$	$6E + 2B + 4D + 3C + 4F$	mol of CH_3 groups
$2E^0 + B^0$	$2E + B + 2D + C + F$	mol of Sn
$2B^0$	$2B + C + 2D$	mol of Cl

Thus:

Methyl balance: $$6E^0 + 2B^0 = 6E + 2B + 4D + 3C + 4F \tag{i}$$

Sn balance: $$2E^0 + B^0 = 2E + B + 2D + C + F \tag{ii}$$

Cl balance: $$2B^0 = 2B + 2D + C \tag{iii}$$

Rearranging (i) yields:

$$6(E^0 - E) + 2(B^0 - B) = 4D + 3C + 4F \tag{iv}$$

Rearranging (ii) yields:

$$2(E^0 - E) + (B^0 - B) = 2D + C + F \tag{v}$$

Rearranging (iii) yields:

$$2(B^0 - B) = 2D + C \tag{vi}$$

and 4 × (v) — (iv) yields:

$$2(E^0 - E) + 2(B^0 - B) = 4D + C \tag{vii}$$

Also (vii) — (vi) yields:

$$2(E^0 - E) = 2D;\ \text{i.e.}\ D = E^0 - E \tag{viii}$$

Further, from (vi) and (viii) one obtains:

$$B = (B^0 - E^0) + E - \tfrac{1}{2}C \tag{ix}$$

which allows the concentration of $(CH_3)_2SnCl_2$ at any time to be calculated from the observation of species not suffering line broadening.

The result most suitable for testing the analysis of the system is eqn. viii, since concentrations D and E may be measured from ^1H NMR peak heights. It is necessary, however, to consider the broadening of the $(CH_3)_4Sn_2Cl_2$ resonance which occurs to an essentially constant extent, by a factor of 1.25—1.3. Thus the slope of a plot of:

$$[(CH_3)_4Sn_2Cl_2]_t \text{ vs. } [(CH_3)_6Sn_2)]_0 - [(CH_3)_6Sn_2]_t$$

would be expected to be ca. 0.8. A sample of such plots is shown in Fig. 3 and details of the observed slopes for the early parts of several reactions are listed in Table 6.

In the early stages of reaction, the plots show good linearity but later, as polymer begins to form, the concentration of $(CH_3)_4Sn_2Cl_2$ begins to be overestimated by the expression under consideration. Nevertheless, for a significant portion of the reaction, the relation has been shown to hold.

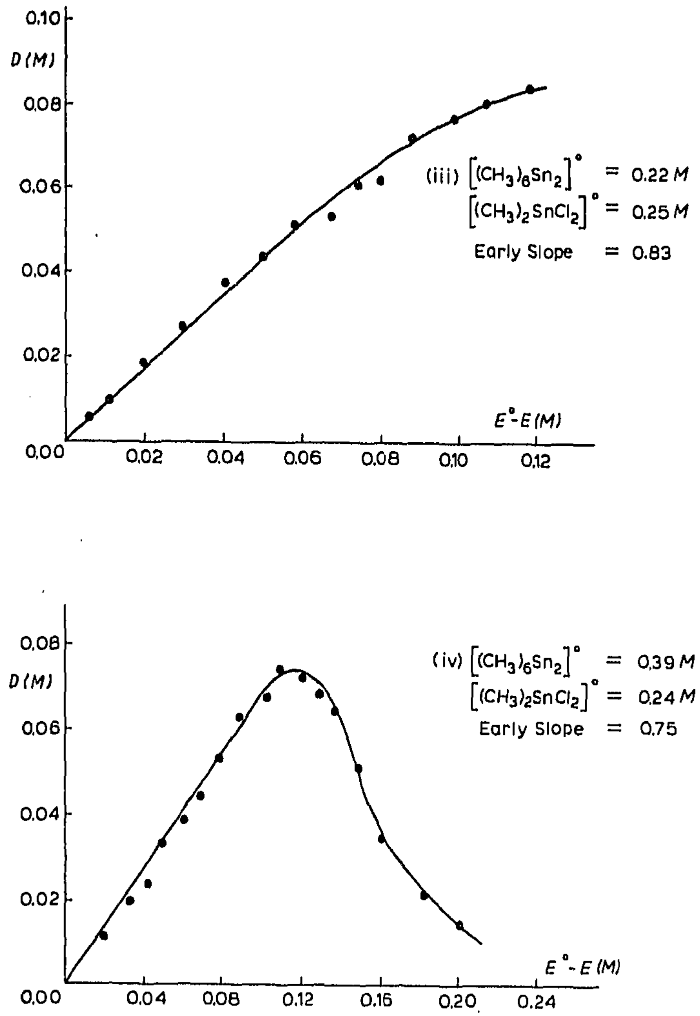


Fig. 3. Plots of D vs. $E^\circ - E$.

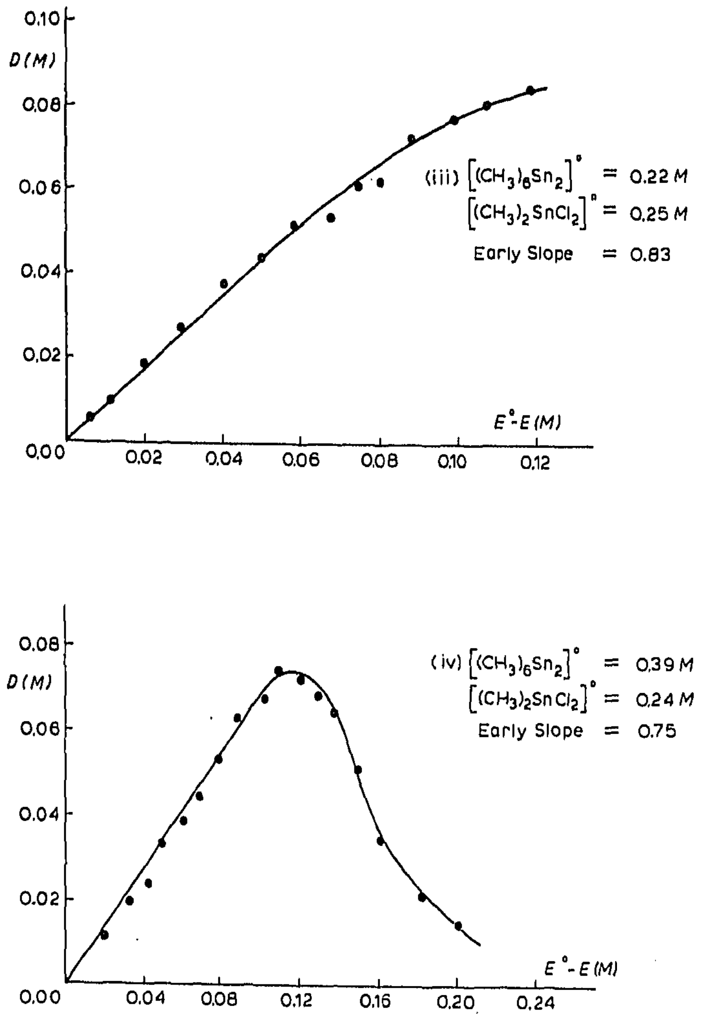


TABLE 6

SLOPES OF PLOTS OF D vs. $E^0 - E$

$[(CH_3)_6Sn_2]^0$ (M)	$[(CH_3)_2SnCl_2]^0$ (M)	Early slope
0.22	0.25	0.83 ± 0.02
0.40	0.48	0.78 ± 0.03
0.18	0.29	0.82 ± 0.03
0.39	0.24	0.75 ± 0.02
0.14	0.16	0.77 ± 0.07

Average slope = 0.79 ± 0.04.

Identification of minor products in solution

The conservation of Sn, Cl and CH_3 groups in solution may be applied, in conjunction with conclusions drawn from chemical shift information, to the assignment of the smaller resonances labelled "telomer" in the ^1H spectra.

The concentration of reagents and hence the molar quantities of Sn, Cl and CH_3 present at the start of reaction were calculated from the weights of reagents added. At a later stage of reaction, (but before any precipitation had occurred) ^1H NMR peak heights were used to estimate quantities of Sn, Cl, and CH_3 accounted for by the major resonances (already assigned). Residual Sn, Cl and CH_3 must, then, be present as compounds giving rise to unassigned resonances. Structures consistent with this elemental composition may be selected from those suggested on the basis of chemical shift.

A reaction mixture analysed in this way consisted of 7.85×10^{-2} g $(CH_3)_6Sn_2$ and 3.31×10^{-2} g $(CH_3)_2SnCl_2$ in a solution of total volume 0.62 ml. Calculated quantities of material present at $t = 0$ are:

No. moles:	CH_3	Sn	Cl
From $(CH_3)_6Sn_2$	1.44×10^{-3}	4.80×10^{-4}	
From $(CH_3)_2SnCl_2$	3.02×10^{-4}	1.51×10^{-4}	3.02×10^{-4}
Total	1.74×10^{-3}	6.31×10^{-4}	3.02×10^{-4}

After 164 min, all of the $(CH_3)_2SnCl_2$ had been consumed and no precipitate had settled out. The concentrations of all identifiable species at that time t are:

No. moles	CH_3	Sn	Cl
From $(CH_3)_6Sn_2$	6.54×10^{-4}	2.18×10^{-4}	
From $(CH_3)_3SnCl$	6.27×10^{-4}	2.09×10^{-4}	2.09×10^{-4}
From $(CH_3)_4Sn_2Cl_2$	2.93×10^{-5}	1.46×10^{-5}	1.46×10^{-5}
From $(CH_3)_4Sn$	9.05×10^{-5}	2.26×10^{-5}	
Total	1.40×10^{-3}	4.75×10^{-4}	2.24×10^{-4}

Unassigned resonances thus arose from 3.40×10^{-4} mol CH_3; 1.56×10^{-4} mol Sn; 0.76×10^{-4} mol Cl corresponding to $CH_3 : Sn : Cl = 4.5 : 2 : 1$.

An expanded ^1H NMR spectrum of the reaction mixture at $t = 164$ min (δ = 0.2—1.1 ppm) is shown in Fig. 4. $(CH_3)_3SnCl$ (C), $(CH_3)_4Sn_2Cl_2$ (D) and $(CH_3)_6Sn_2$ (E) are readily identifiable. The region = 0.3—1.1 ppm is illustrated schematically in Fig. 5.

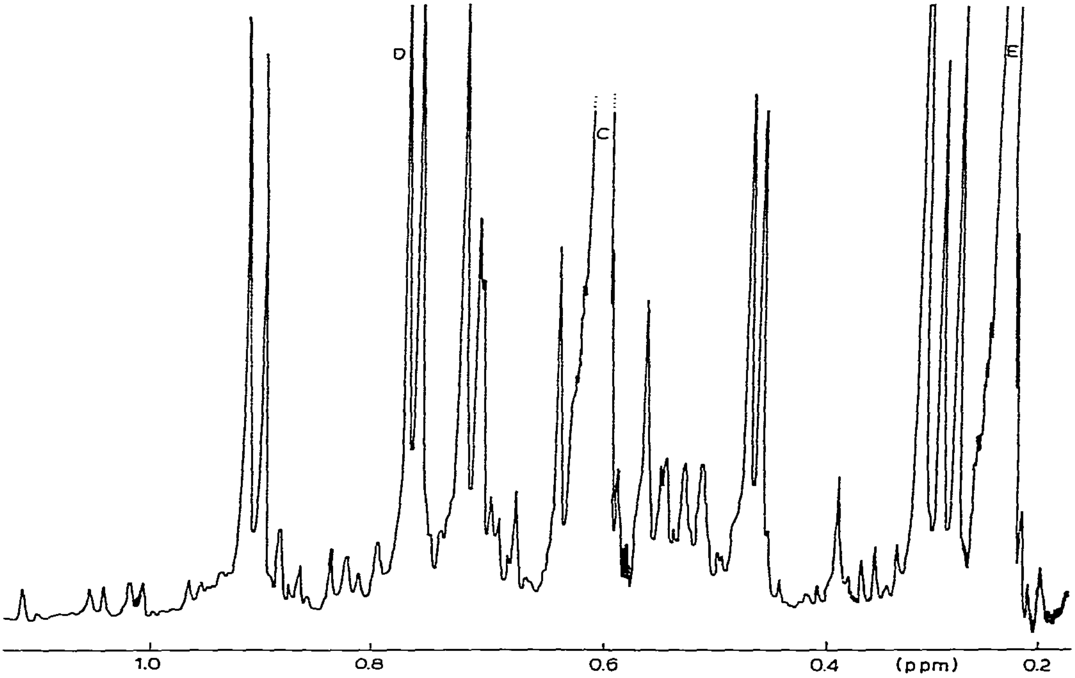


Fig. 4. Expanded ^{1}H NMR spectrum of reaction mixture: $(CH_3)_2SnCl_2$ (0.24 *M*) + $(CH_3)_6Sn_2$ (0.39 *M*); *t* = 164 min.

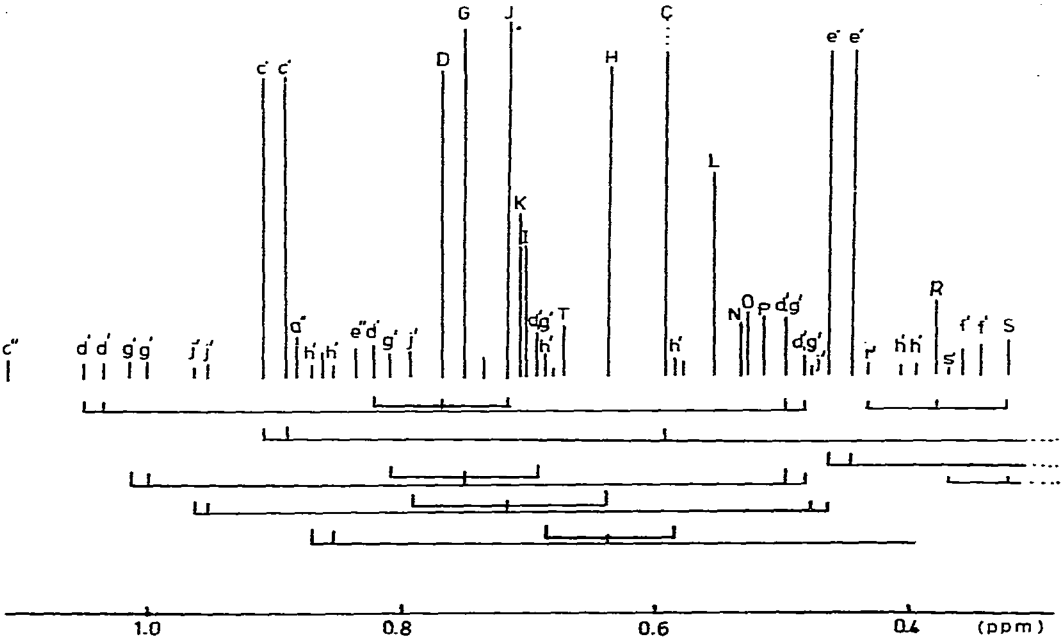


Fig. 5. Schematic representation of the ^{1}H NMR spectrum shown in Fig. 4.

TABLE 7

UNASSIGNED RESONANCES IN ^{1}H NMR SPECTRUM, Fig. 5.

Peak	Chemical Shift (ppm)	^2J(Sn—H) (Hz)	^3J(Sn—H) (Hz)
G	0.76	52.1, 54.5	12.6
H	0.63	47.5, 50.4	12.1
I	0.71		
J	0.72	47.4, 50.8	
K	0.70		
L	0.55		
N	0.53		
O	0.52		
P	0.50		
R	0.36		11.3
S	0.31		11.7
T	0.67		

Table 7 lists chemical shifts and, where observed, coupling constants for the remaining resonances G—T, and tentative assignments are given in Table 8. These are based upon the known chemical shifts for C, D and E together with the data reported by Brown and Morgan [15] and reasonable estimates of the chloro-group effects.

It seems unlikely that $(CH_3)_5Sn_2Cl$ (I) will be observed in this spectrum as it was never observed in spectra of the $(CH_3)_3SnCl/(CH_3)_6Sn_2$ or other systems. It is more likely that resonances L and I arise from $(CH_3)_7Sn_3Cl$ (II) with the feature from CH_3 groups attached to the central Sn being obscured by $(CH_3)_3SnCl$.

Comparison of the heights of appropriate resonances allows an estimation of the relative amounts of each of the compounds II—VII present in the mixture. Table 9 lists these quantities and the relative amounts of Sn, Cl and CH_3 in the 'missing' part of the total mixture can be evaluated as in Table 10.

The resultant ratio of CH_3 : Sn : Cl obtained in this way is 4.3 : 2.1 : 1 which is in excellent agreement with the ratio 4.5 : 2 : 1 observed and thus the tentative assignments listed in Table 8 appear to be essentially correct.

It is important to note that the formation of all of the chlorine-containing compounds suggested may be explained by successive insertions of $(CH_3)_2Sn$ into Sn—Cl bonds of species present in high concentration in the reaction mixture in accordance with the mechanism suggested for the build-up of polymer in these systems [5,14].

Reaction of $(CH_3)_6Sn_2$ with $(CD_3)_2SnCl_2$

In order to further investigate the "exchange" process occurring in the $(CH_3)_2SnCl_2/(CH_3)_6Sn_2$ reaction system and to investigate the mechanism of formation of $(CH_3)_4Sn_2Cl_2$, the reaction of $(CH_3)_6Sn_2$ with perdeuterodimethyltin dichloride was examined. The progress of a reaction of $(CH_3)_6Sn_2$ (0.12 *M*) and $(CD_3)_2SnCl_2$ (0.09 *M*), in methanol at 30°C was monitored by ^{1}H NMR. It was observed that, soon after reaction had commenced, a small, broad resonance corresponding to $(CH_3)_2SnCl_2$ was present. This peak grew slightly as reaction proceeded then diminished and eventually disappeared.

TABLE 8

TENTATIVE ASSIGNMENTS OF RESONANCES G—T (Fig. 5)

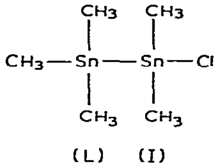
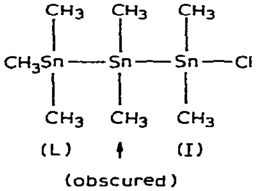
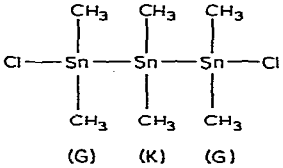
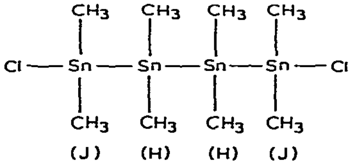
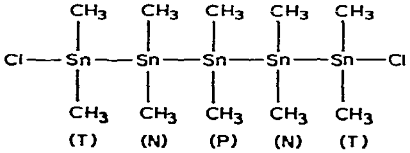
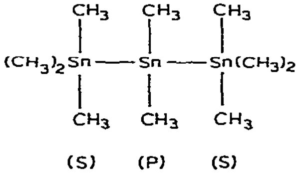
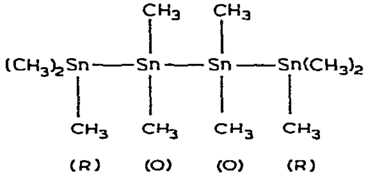
Resonances	Compound	Compound No.
L, I	 $CH_3-\overset{CH_3}{\underset{CH_3}{Sn}}-\overset{CH_3}{\underset{CH_3}{Sn}}-Cl$	I
or L, I	 $CH_3\overset{CH_3}{\underset{CH_3}{Sn}}-\overset{CH_3}{\underset{CH_3}{Sn}}-\overset{CH_3}{\underset{CH_3}{Sn}}-Cl$	II
G, K	 $Cl-\overset{CH_3}{\underset{CH_3}{Sn}}-\overset{CH_3}{\underset{CH_3}{Sn}}-\overset{CH_3}{\underset{CH_3}{Sn}}-Cl$	III
J, H	 $Cl-\overset{CH_3}{\underset{CH_3}{Sn}}-\overset{CH_3}{\underset{CH_3}{Sn}}-\overset{CH_3}{\underset{CH_3}{Sn}}-\overset{CH_3}{\underset{CH_3}{Sn}}-Cl$	IV
N, P, T	 $Cl-\overset{CH_3}{\underset{CH_3}{Sn}}-\overset{CH_3}{\underset{CH_3}{Sn}}-\overset{CH_3}{\underset{CH_3}{Sn}}-\overset{CH_3}{\underset{CH_3}{Sn}}-\overset{CH_3}{\underset{CH_3}{Sn}}-Cl$	V
S, P	 $(CH_3)_2\overset{CH_3}{\underset{CH_3}{Sn}}-\overset{CH_3}{\underset{CH_3}{Sn}}-\overset{CH_3}{\underset{CH_3}{Sn}}(CH_3)_2$	VI
R, O	 $(CH_3)_2\overset{}{\underset{CH_3}{Sn}}-\overset{CH_3}{\underset{CH_3}{Sn}}-\overset{CH_3}{\underset{CH_3}{Sn}}-\overset{}{\underset{CH_3}{Sn}}(CH_3)_2$	VII

TABLE 9

RELATIVE PROPORTIONS OF COMPOUNDS II—VII PRESENT IN SYSTEM

Compound No.	Formula	Relative Amount
II	$(CH_3)_7Sn_3Cl$	5.7
III	$(CH_3)_6Sn_3Cl_2$	15.3
IV	$(CH_3)_8Sn_4Cl_2$	15.6
V	$(CH_3)_{10}Sn_5Cl_2$	2.3
VI	$(CH_3)_8Sn_3$	1.0
VII	$(CH_3)_{10}Sn_4$	2.2

A yellow-orange polymer was produced and its mass spectrum recorded. The appearance of this spectrum was markedly different from that of spectra of yellow polymers from the reaction systems $(CH_3)_2SnCl_2/(CH_3)_6Sn_2$, $(CH_3)_3SnCl/(CH_3)_6Sn_2$ and $(CD_3)_3SnCl/(CH_3)_6Sn_2$, all of which are quite similar. In the spectrum of the polymer from $(CD_3)_2SnCl_2/(CH_3)_6Sn_2$, considerable perturbation of the characteristic isotope patterns is observed. As an excess of $(CH_3)_6Sn_2$ was employed in this reaction, it is known that this precipitate must be comprised of unchlorinated methylated polystannanes. Thus, the difference between this and other spectra must arise from the incorporation of CD_3 groups into the polymer. This is in marked contrast to the effect of reacting $(CD_3)_3SnCl$ with $(CH_3)_6Sn_2$, where no deuterium incorporation is observed.

In order that this spectrum may be fully analysed, one must assume that no scrambling of ^{1}H and ^{2}D has occurred in the mass spectrometer, i.e. that, where in the other spectra a fragment $(CH_3)_xSn_y$ is observed, what is observed here is simply a cluster of fragments $(CH_3)_{x-z}(CD_3)_zSn_y$. Given this assumption, the relative amounts of fragments $(CH_3)_{x-1}(CD_3)Sn_y$, $(CH_3)_{x-2}(CD_3)_2Sn_y$ etc. may be determined. The results of this analysis of the spectrum are listed in Table 11. Deuterium-labelled fragments containing up to seven atoms of Sn are observed. The 'combined intensity' for each fragment Me_xSn_y (Me = CH_3 or CD_3) may also be calculated and the spectrum so obtained is quite similar to those previously observed, which serves to satisfy the assumption that this polymer contains compounds of the same type as seen in other "dimethylstannane" polymers.

TABLE 10

RELATIVE AMOUNTS OF Sn, Cl, CH_3 PREDICTED BY PROPOSED MIXTURE

No. units of:	CH_3	Sn	Cl
From $(CH_3)_7Sn_3Cl$	39.9	17.1	5.7
From $(CH_3)_6Sn_3Cl_2$	91.8	45.9	30.6
From $(CH_3)_8Sn_4Cl_2$	124.8	62.4	31.2
From $(CH_3)_{10}Sn_5Cl_2$	23.C	11.5	4.6
From $(CH_3)_8Sn_3$	8.0	3.0	0.0
From $(CH_3)_{10}Sn_4$	22.0	8.8	0.0
Total	309.5	148.7	72.1

TABLE 11

MASS SPECTRUM OF POLYMER EX $(CD_3)_2SnCl_2$ (0.09 *M*) + $(CH_3)_6Sn_2$ (0.12 *M*)

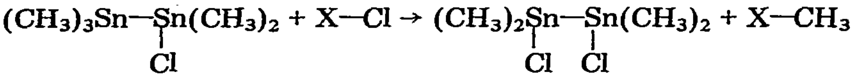
m/e	Probable ion	Relative intensity	*m/e*	Probable ion	Relative intensity
1066	$(CH_3)_{12}(CD_3)_3Sn_7^+$	2.7	632	$(CH_3)_8(CD_3)_2Sn_4^{+\cdot}$	30.8
1051	$(CH_3)_{11}(CD_3)_3Sn_7^{+\cdot}$	6.6	629	$(CH_3)_9CD_3Sn_4^{+\cdot}$	39.3
1048	$(CH_3)_{12}(CD_3)_2Sn_7^{+\cdot}$	9.2	626	$(CH_3)_{10}Sn_4^{+\cdot}$	50.5
1036	$(CH_3)_{10}(CD_3)_3Sn_7^+$	5.2	617	$(CH_3)_7(CD_3)_2Sn_4^+$	73.7
934	$(CH_3)_{10}(CD_3)_4Sn_6^+$	8.4	614	$(CH_3)_8CD_3Sn_4^+$	49.9
928	$(CH_3)_{12}(CD_3)_2Sn_6^+$	7.2	611	$(CH_3)_9Sn_4^+$	57.6
898	$(CH_3)_{10}(CD_3)_2Sn_6^{+\cdot}$	23.5	602	$(CH_3)_6(CD_3)_2Sn_4^{+\cdot}$	22.6
895	$(CH_3)_{11}CD_3Sn_6^{+\cdot}$	32.9	599	$(CH_3)_7CD_3Sn_4^{+\cdot}$	46.1
883	$(CH_3)_9(CD_3)_2Sn_6^+$	23.2	596	$(CH_3)_8Sn_4^{+\cdot}$	42.7
880	$(CH_3)_{10}CD_3Sn_6^+$	13.1	587	$(CH_3)_5(CD_3)_2Sn_4^+$	46.8
780	$(CH_3)_{10}(CD_3)_2Sn_5^+$	29.6	584	$(CH_3)_6CD_3Sn_4^+$	52.7
774	$(CH_3)_{12}Sn_5^{+\cdot}$	36.8	581	$(CH_3)_7Sn_4^+$	26.3
762	$(CH_3)_{10}CD_3Sn_5^+$	46.4	557	$(CH_3)_3(CD_3)_2Sn_4^+$	31.5
759	$(CH_3)_{11}Sn_5^+$	50.5	554	$(CH_3)_4CD_3Sn_4^+$	20.2
753	$(CH_3)_7(CD_3)_3Sn_5^{+\cdot}$	11.4	551	$(CH_3)_5Sn_4^+$	29.9
747	$(CH_3)_9CD_3Sn_5^{+\cdot}$	54.1	527	$CH_3(CD_3)_2Sn_4^+$	12.6
744	$(CH_3)_{10}Sn_5^{+\cdot}$	56.0	524	$(CH_3)_2CD_3Sn_4^+$	10.2
735	$(CH_3)_7(CD_3)_2Sn_5^+$	49.2	521	$(CH_3)_3Sn_4^+$	19.6
729	$(CH_3)_9Sn_5^+$	38.6	509	$CH_3CD_3Sn_4^{+\cdot}$	28.6
714	$(CH_3)_8Sn_5^{+\cdot}$	10.7	506	$(CH_3)_2Sn_4^{+\cdot}$	17.9
702	$(CH_3)_6CD_3Sn_5^+$	29.1	494	$CD_3Sn_4^+$	13.9
699	$(CH_3)_7Sn_5^+$	6.6	491	$CH_3Sn_4^+$	31.3
678	$(CH_3)_2(CD_3)_3Sn_5^+$	0.9	467	$(CH_3)_5(CD_3)_2Sn_3^+$	96.8
675	$(CH_3)_3(CD_3)_2Sn_5^+$	2.8	464	$(CH_3)_6CD_3Sn_3^+$	100.0
672	$(CH_3)_4CD_3Sn_5^+$	2.8	461	$(CH_3)_7Sn_3^+$	73.5
669	$(CH_3)_5Sn_5^+$	4.7	452	$(CH_3)_4(CD_3)_2Sn_3^+$	72.9
449	$(CH_3)_5CD_3Sn_3^+$	29.4	407	$CH_3(CD_3)_2Sn_3^+$	18.4
446	$(CH_3)_6Sn_3^{+\cdot}$	61.4	404	$(CH_3)_2CD_3Sn_3^+$	24.6
437	$(CH_3)_3(CD_3)_2Sn_3^+$	31.7	401	$(CH_3)_3Sn_3^+$	30.8
434	$(CH_3)_4CD_3Sn_3^+$	20.3	392	$(CD_3)_2Sn_3^{+\cdot}$	9.7
431	$(CH_3)_5Sn_3^+$	26.0	389	$CH_3CD_3Sn_3^{+\cdot}$	18.9
422	$(CH_3)_2(CD_3)_2Sn_3^+$	11.3	386	$(CH_3)_2Sn_3^{+\cdot}$	25.0
419	$(CH_3)_3CD_3Sn_3^{+\cdot}$	13.8	371	$CH_3Sn_3^+$	37.2
416	$(CH_3)_4Sn_3^{+\cdot}$	27.0	356	$Sn_3^{+\cdot}$	18.5

Two important conclusions are thus drawn from this reaction:

(i) Methyl groups originally present as $(CH_3)_6Sn_2$ have appeared as $(CH_3)_2SnCl_2$ and;

(ii) CD_3 groups originally present as $(CD_3)_2SnCl_2$ have appeared as polymer.

This reaction is also significant as it provides information on the mechanism of formation of $(CH_3)_4Sn_2Cl_2$ in the reaction of $(CH_3)_2SnCl_2$ with $(CH_3)_6Sn_2$. There are two pathways for formation of this compound (assuming that the first step involves Sn—C and not Sn—Sn cleavage). Firstly, it may be formed by further attack of initially formed $(CH_3)_5Sn_2Cl$ by some electrophile, thus:



$$(CH_3)_3Sn{-}\underset{\displaystyle Cl}{\underset{|}{Sn}}(CH_3)_2 + X{-}Cl \rightarrow (CH_3)_2\underset{\displaystyle Cl}{\underset{|}{Sn}}{-}\underset{\displaystyle Cl}{\underset{|}{Sn}}(CH_3)_2 + X{-}CH_3$$

X—Cl = some electrophile,
e.g. $(CH_3)_2SnCl_2$
$(CH_3)_3SnCl$
$(CH_3)_4Sn_2Cl_2$

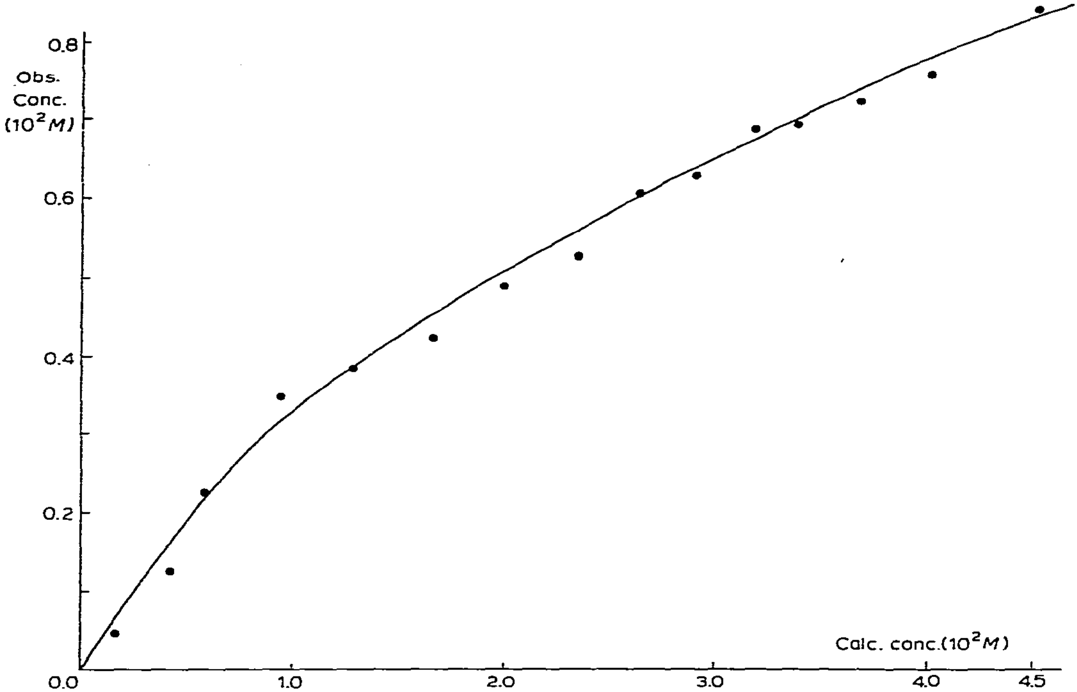
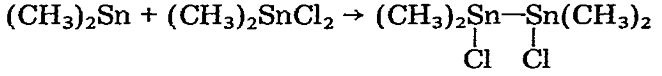


Fig. 6. Plot of "observed" vs. "calculated" concentrations of $(CH_3)_4Sn_2Cl_2$ for reaction: $(CD_3)_2SnCl_2$ (0.09 M) + $(CH_3)_6Sn_2$ (0.12 M).

Secondly, it may be formed exclusively by insertion of $(CH_3)_2Sn$ into a Sn—Cl bond in $(CH_3)_2SnCl_2$, thus:



$$(CH_3)_2Sn + (CH_3)_2SnCl_2 \rightarrow (CH_3)_2\underset{\mathrm{Cl}}{\underset{|}{Sn}}-\underset{\mathrm{Cl}}{\underset{|}{Sn}}(CH_3)_2$$

The second path appears the more likely of the two for several reasons. It is known that $(CH_3)_5Sn_2Cl$ is a highly reactive species, decomposing so readily as to never reach an appreciable concentration in any reaction mixture studied so far. It is most unlikely that the electrophilic displacement of a methyl group from this compound could, at least under these reaction conditions, proceed at a rate faster than that of its decomposition; a factor necessary for the first path to be viable. The $(CD_3)_2SnCl_2$ reaction provides proof of this hypothesis since the extent of incorporation of deuterium into $(CH_3)_4Sn_2Cl_2$ distinguishes the two pathways for its formation and subsequent exchange reactions. If the first path is followed, the initially formed $Me_4Sn_2Cl_2$ (where Me describes methyl groups which may be CH_3 or CD_3) will contain no deuterium. Subsequent exchanges will give rise, later in the reaction, to some deuterium incorporation. However, if the second path is followed, then the $Me_4Sn_2Cl_2$ formed will immediately contain 50% deuterium and will continue to be enriched with deuterium as reaction proceeds.

The extent of enrichment may be studied by use of the previously determined stoichiometric result (eq. viii)

$$[(CH_3)_4Sn_2Cl_2]_t = [(CH_3)_6Sn_2]_0 - [(CH_3)_6Sn_2]_t$$

A plot of 'observed' vs. 'calculated' concentration of $Me_4Sn_2Cl_2$, where the 'observed' concentration is the concentration measured from ^1H NMR peak height at time t and the 'calculated' concentration is obtained from eq. viii affords a measure of incorporation of deuterium into $Me_4Sn_2Cl_2$. Such a plot is shown in Fig. 6. The curve obtained has, during the early stages of reaction, a slope of 0.37 which levels off to ca. 0.15 later. After correction for the broadening of the $Me_4Sn_2Cl_2$ resonance (by multiplying by a factor of 1.27) the slope thus varies from 0.49—0.20. The slope of 0.49 during the early stages of reaction corresponds to a level of 50% incorporation of deuterium into $Me_4Sn_2Cl_2$. This later increases to a value of ca. 80%, although this is probably an overestimate as such plots have already been shown to exhibit some departure from linearity during the later stages of reaction. Thus early on in the reaction, $Me_4Sn_2Cl_2$ contains 50% deuterium which is the result expected for an insertion of $(CH_3)_2Sn$ into $(CD_3)_2SnCl_2$ as the sole route to this intermediate.

Precipitate diversity

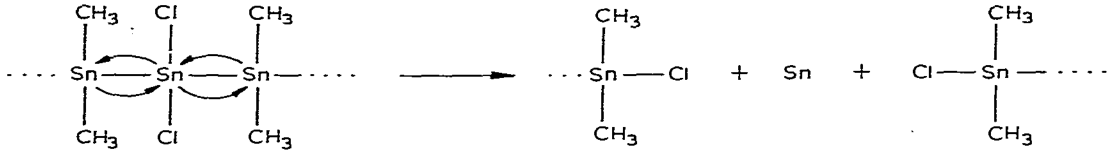
The nature of the precipitate produced in a $(CH_3)_2SnCl_2/(CH_3)_6Sn_2$ reaction system exhibits a dependence on the ratio $r = [(CH_3)_2SnCl_2]_0/[(CH_3)_6Sn_2]_0$ such that $r < 2$: yellow, chlorine-free polymer; $2 < r < 3$: white, chlorinated polymer; $r > 3$: metallic tin.

This difference may be understood by a consideration of the species that are present in high concentration at the time when precipitate begins to appear, as judged by the concentration/time curves for reactions with $r = 0.62$ and 2.13, respectively. (See Figs. 2 and 4 of our following paper [14]).

In the first case, ($r = 0.62$), substantial quantities of both $(CH_3)_6Sn_2$ and $(CH_3)_3SnCl$ are present late in the reaction, while only small amounts of the other principal chlorine-containing species $(CH_3)_2SnCl_2$ and $(CH_3)_4Sn_2Cl_2$ remain. Chlorinated species $(CH_3)_{2n+1}Sn_nCl$ and $(CH_3)_{2n}Sn_nCl_2$ thus still have a methyl-group source, $(CH_3)_6Sn_2$, with which to react and become fully methylated before precipitation occurs. The reaction of residual $(CH_3)_6Sn_2$ with $(CH_3)_3SnCl$ also produces a chlorine-free product.

In the second case ($r = 2.13$) a very different situation obtains late in the reaction. Very little $(CH_3)_6Sn_2$ or $(CH_3)_4Sn$ remains, while $(CH_3)_2SnCl_2$, $(CH_3)_3SnCl$ and $(CH_3)_4Sn_2Cl_2$ are all present in substantial amounts. A complex set of equilibria will develop. $(CH_3)_2Sn$, generated at this stage primarily via dissociation of $(CH_3)_4Sn_2Cl_2$ (which eventually disappears) will insert into Sn—Cl bonds in chlorinated intermediates and build up their chain length. Chain lengths will, on the other hand, be decreased by extrusions of $(CH_3)_2Sn$. When, as in the previous case, methyl group sources are present, these equilibria are disturbed by methylation of chlorine-containing compounds with the driving force being provided by precipitation of fully methylated compounds. Now, when deprived of a methyl group source, $(CH_3)_{2n+1}Sn_nCl$ and $(CH_3)_{2m}Sn_mCl_2$ may not only maintain their Cl content but also reach sufficient chain length and high enough concentration for precipitation. In addition, any fully methylated compounds which do form are formed in the presence of large amounts of $(CH_3)_3SnCl$, $(CH_3)_2SnCl_2$ etc. and may thus be demethylated.

Still larger quantities of $(CH_3)_2SnCl_2$ etc. remain when a larger excess of $(CH_3)_2SnCl_2$ (>3 : 1) is employed at the beginning of the reaction and intermediates containing several chlorine atoms may then be produced. If compounds with two chlorine atoms on one tin are formed, these may extrude metallic Sn by a process such as



The occurrence of such a process in reactions of certain organoplumbanes has previously been suggested by Arnold [8]. These *gem*-dichloro compounds may be formed by any compound containing two chloro-groups via methyl shifts. Again a precipitation (this time of metallic tin) provides the driving force for disturbance of solution equilibria in the direction of formation of a particular insoluble product.

The intermediacy of $(CH_3)_2Sn$ and the availability, late in the reaction, of methyl group sources and/or demethylating agents thus serve to explain the diversity of precipitates which may be produced by a $(CH_3)_2SnCl_2/(CH_3)_6Sn_2$ reaction mixture.

Acknowledgements

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References

1 G. Tagliavini, G. Pilloni and G. Plazzogna, Ric. Sci., 36 (1966) 114.
2 G. Tagliavini, G. Pilloni and G. Plazzogna, Ric. Sci., 36 (1966) 3.
3 D.C. McWilliam and P.R. Wells, J. Organometal. Chem., 85 (1975) 165.
4 D.P. Arnold and P.R. Wells, J. Organometal. Chem., 108 (1976) 345.
5 D.P. Arnold, M.J. Cuthbertson and P.R. Wells, J. Organometal. Chem., 184 (1980) 39.
6 C.A. Kraus and W.V. Sessions, J. Amer. Chem. Soc., 47 (1925) 2361.
7 D.C. McWilliam, Thesis, University of Queensland 1973.
8 D.P. Arnold, Thesis, University of Queensland, 1975.
9 W.F. Edgell and C.H. Ward, J. Amer. Chem. Soc., 76 (1954) 1169.
10 K.A. Kozeschkow, Chem. Ber., 66B (1933) 1661.
11 H. Lund and J. Bjerrum, Ber. Deut. Chem. Ges., 64 (1931) 210.
12 M.J. Cuthbertson and P.R. Wells, J. Org. Chem., in press.
13 B. Mathiasch, Inorg. Nuc. Chem. Lett., 13 (1977) 13.
14 M.J. Cuthbertson and P.R. Wells, J. Organometal. Chem., 216 (1981) 349.
15 T.L. Brown and G.L. Morgan, Inorg. Chem., 2 (1963) 736.